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THE ADSORPTION OF OLEIC ACID ON HEMATITE AS INFLUENCED BY pH - A RADIOMETRIC STUDY

by

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INTRODUCTION

The adsorption of fatty acids on metallic oxides has been the subject of extensive studies, and several theories have been proposed to explain the stability of the adsorbed films.

It was thought that a measurement of the amounts of oleic acid adsorbed on pure hematite at various concentrations and pH, and of the fractions of the adsorbed films remaining on the mineral after drastic extraction with an organic solvent, might provide some information on the nature of the attachment of the oleic acid molecule at the hematite surface.

MATERIALS AND EXPERIMENTAL PROCEDURE

A high-grade sample of specular hematite, obtained from the Quebec-Cartier Mining Corporation Ltd., was crushed and

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screened, and the -100 + 200 mesh fraction was cleaned on a magnetic separator in order to remove the quartz and the other gangue minerals. Several washings with dilute hydrochloric acid, followed by a washing in a dilute hydrogen peroxide solution, produced a slime-free hematite containing less than 0.5 per cent quartz (by microscopic examination).

The benzene solution of oleic acid was prepared by dissolving 0.308 g purified oleic acid (Fisher) in 250 ml purified benzene and adding 0.2 mc oleic acid-1-C14 (Radiochemical Centre, Amersham). Sulfuric acid and sodium hydroxide were used to adjust the pH of the water.

In the adsorption tests, 10-gram samples of hematite were agitated for 20 minutes in 10 ml water containing amounts of oleic acid varying from 62.5 to 1230 micrograms. Because of the low solubility of oleic acid in water, emulsions of the acid in water were prepared by pipetting into a glass vial the required amount of oleic acid in benzene, evaporating the solvent in a draft, adding 10 ml water at the required pH, and emulsifying by ultrasonic agitation.

After agitation, the samples were centrifuged, and a 0.250 ml sample of the supernatant liquid was taken for the measurement of the residual oleic acid. The hematite was filtered from the solution in a Gooch crucible, washed with 50 ml water at the pH of contaction, and dried at 85°C.

The dry hematite was then split into four 2.5 g fractions, two of which were counted under a thin window Geiger tube, for the determination of the amount of oleic acid adsorbed.

The other two fractions were mixed and extracted with benzene in a micro Soxhlet apparatus for a period of one hour. After extraction, the activity remaining on the hematite was measured under the Geiger tube, and the activity extracted with the benzene was measured by liquid scintillation counting. The radiometric equipment used for these measurements and the method used for correlating the results obtained by counting the solid and liquid samples have been described in an earlier report (1).

Surface Area of the Hematite, -100 + 200 mesh

The surface area of the -100 + 200 mesh fraction of hematite used in these tests was measured by the B.E.T. method, using krypton instead of nitrogen as the adsorbed gas. Measurements on two representative samples gave a surface area of 475 cm^2/gram.

RESULTS AND DISCUSSION

Adsorption

Figure 1 shows the adsorption of oleic acid as a function of the initial amount at constant pH. Figure 2 is a plot of the same results, but as a function of the pH at constant initial amounts of oleic acid.

On Figure 1, the adsorption is seen to be proportional to the amount of oleic acid initially present, over the range of concentration studied. It should be pointed out that the duration of the contaction, 20 minutes, is much longer than required for equilibrium, even at the lowest acid concentration

used.

Figure 2 shows more clearly the pH range (3.5 to 8.0), in which the adsorption is practically constant for a given initial amount of oleic acid. The abrupt inflexion in the curves at approximately pH 8.5 seems to agree well with a recently published value of pH 8.5 for the zero point of charge of hematite.

Desorption

The physical and chemical properties of metallic soaps such as Fe-oleate are little known because of the difficulty in preparing these compounds in a pure state. Bulk metallic soaps, always containing an excess of free acid, are soluble in boiling xylene or benzene, but soaps formed at the surface of metals are not readily dissolved, even in boiling solvents. It has been shown by infra-red absorption that the binding between the oleate radical and the calcium atom at the surface of CaF_2 is quite different from the one existing in calcium oleate.

In order to evaluate the proportion of oleic acid that might be physically attached, thus readily soluble in benzene, five-gram samples of hematite contacted with oleic acid, at the pH values and acid concentrations already mentioned, were extracted with benzene for a period of one hour, previous tests having shown complete extraction during this time. Figure 3 shows the rather unusual results obtained. As the pH increases, the fraction of oleic acid extracted decreases until pH 5.0 is reached, then shows a maximum of extraction near pH 6, followed

by a fairly uniform decrease of extraction with increasing pH. Previous experiments had shown that a significant amount of Fe was present in some benzene extracts. More-accurate determinations were made of the Fe content of the benzene extracts from hematite that had been contacted with the highest concentration of oleic acid. The determinations were made using the ortho-phenanthroline method with a Type B Beckman Spectrophotometer. Fe determinations were made by Miss E. Mark, Analytical Chemistry Subdivision, Mineral Sciences Division. The results, expressed so as to account for the amount of oleic acid present in a Fe mono-oleate (≈15 per cent Fe), are shown in Figure 4, along with the corresponding extraction curve. Although the accuracy of such measurements is poor, because of the small Fe content of the oleate and the uncertainty of the formula of this soap, one can see that, by subtracting the contribution of the oleate from the total per cent oleic acid extracted, one can obtain a fairly uniform decrease in extraction of oleic acid with increasing pH. Similar results were obtained by Peck (2) and others on fluorite, using infra-red absorption for the determination of physically absorbed oleic acid and chemisorbed oleate.

CONCLUSION

A comparison of the results obtained on adsorption and extraction over the range of pH studied leads to the following conclusions.

At low pH, because of the high hydrogen ion concentration, the oleic acid is presented in an undissociated form, either

as molecules or as micelles, and the adsorption on the hematite is low, is mostly physical, and the adsorbed film is easily extractable.

As the pH of the medium increases, dissociation of the oleic acid results in chemisorption, coupled with the formation of hemi-micelles at the adsorbing surface. This results in a solubilization of some of the surface oleate, as evidenced by the benzene extraction of some Fe-oleate.

When pH 8.5 is reached, the high concentration of sodium ions, together with the low reactive property of the hematite near its zero point of charge, drastically reduces both physical and chemical adsorption.

The second phase of this work, now in progress, will consist of a series of flotation tests and a study of the physically and chemically adsorbed oleic acid on the flotation products. Similar work on cassiterite has shown that the total amount of oleic acid adsorbed on the mineral is not necessarily a criterion for floatability, but that the nature of the adsorption has to be considered.

REFERENCES

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2. A.S. Peck, Infrared Studies of Oleic Acid and Sodium Oleate Adsorption on Fluorite, Barite and Calcite, U.S. Bur. Mines, Rept. Invest. No. 6202, 16 pp. (1963).

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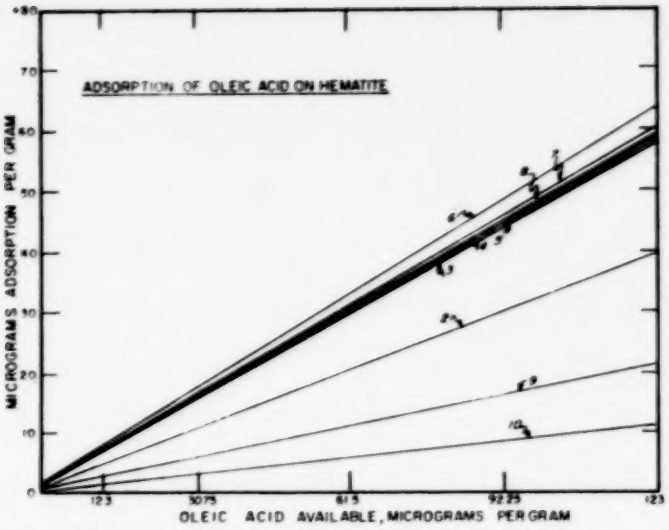

Figure 1

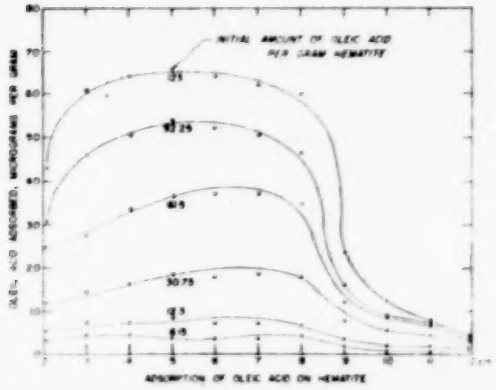

Figure 2

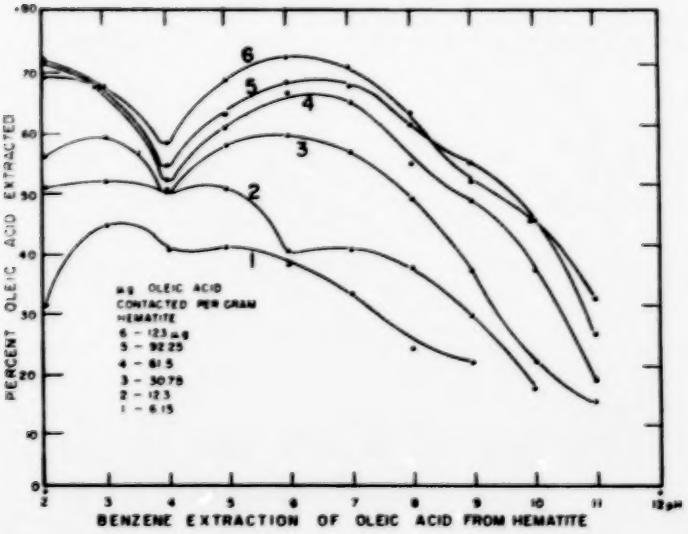
PERCENT OLEIC ACID EXTRACTED
BENZENE EXTRACTION OF OLEIC ACID FROM HEMATITE
μg OLEIC ACID CONTACTED PER GRAM HEMATITE
6 - 123 μg
5 - 92.25
4 - 61.5
3 - 30.75
2 - 12.3
1 - 6.15

Figure 3

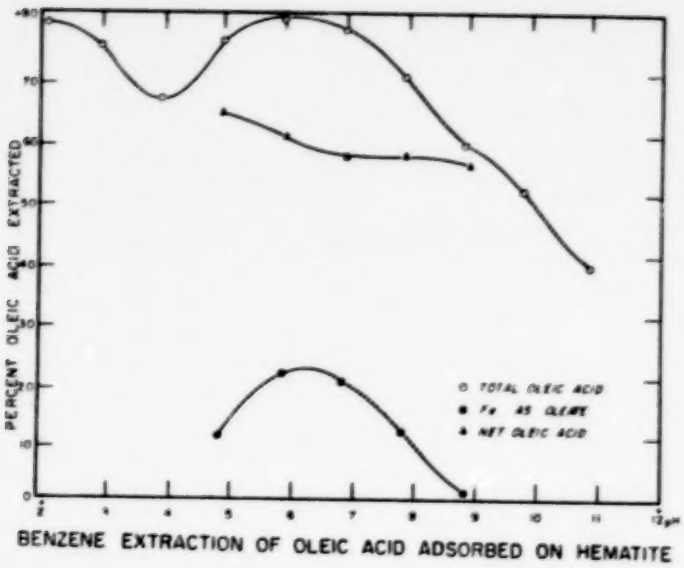
PERCENT OLEIC ACID EXTRACTED
TOTAL OLEIC ACID
NET OLEIC ACID
BENZENE EXTRACTION OF OLEIC ACID ADSORBED ON HEMATITE

Figure 4